

ADVANCES IN UNDERSTANDING NATURAL GROUNDWATER QUALITY CONTROLS IN COASTAL AQUIFERS

K. WALRAEVENS✉ and M. VAN CAMP

Laboratory for Applied Geology and Hydrogeology – Ghent University, Krijgslaan 281, S8, 9000 Gent, Belgium,
E-mail: Kristine.Walraevens@UGent.be

Abstract

Groundwater quality in coastal aquifers is largely influenced by the interaction between the sea and the bordering aquifer systems. This interaction can result in freshening of saline aquifers or salinization of fresh water bodies. In complex cases even both situations can be found in the same aquifer system. While the main mechanism for salinization or freshening is hydrodynamically driven (groundwater flow), also physical and chemical processes within the aquifer will alter groundwater composition. Cation exchange is in many cases an important process to consider; it results in a hydrochemical spectrum of groundwater types reflecting both the hydrodynamical and hydrochemical characteristics of the aquifer.

In order to understand the natural groundwater quality and the controlling processes in a coastal aquifer, it is crucial to know both the hydrodynamical and hydrochemical behaviour and the way these are linked together, because usually only the interaction between them can explain the observed quality distributions. Where mixing of fresh and salt water occurs, density-driven flow may become important and change quality distribution, while the groundwater composition itself influences hydrodynamics. An integrated approach of both aspects is indispensable.

Modelling is an important tool in understanding how aquifer systems work. Until recently, hydrodynamical and hydrochemical aspects were tackled separately, with different models. Hydrodynamical aspects have been studied with flow models (such as MODFLOW) or a combination of a flow and a solute transport model (such as MT3D) for simulating salt transport, coupled together for incorporating density-driven flow (such as in SEAWAT). On the other hand, hydrochemical aspects have been investigated with hydrogeochemical models based on speciation and a reaction scheme. In hydrogeochemical models, groundwater flow was either not taken into account, or, at best, it was considered in a very simplified approach (along a path-line). Recently, codes have been developed combining three-dimensional flow models fully with the flexibility of an extensible hydrochemical model based on thermodynamic databases, such as PHAST, which combines the well-known PHREEQC model with the HST3D model for flow and

✉ Corresponding author

transport. Simulations with the PHAST model have shown that it is capable of simulating the whole hydrochemical spectrum of groundwater types in coastal aquifers under freshening and salinizing conditions incorporating cation exchange processes and mineral equilibria such as calcite dissolution. The capabilities of this new generation of models will also allow for including redox components (iron content of the water) or processes such as surface complexation (e.g. sorption onto hydroxides). The future for such models looks bright, because for the first time they will provide the complete groundwater composition as their output.

However, models need to be based on good and sufficient field data! Without them the reliability of the models is unknown and their value for predictive purposes is hypothetical. Therefore the advances in modelling should go together with new techniques of sampling, measuring and monitoring and with improved analytical methods. Advances have been made also in these fields.

Yet, the most important advance in understanding natural groundwater quality is not related to a specific technical innovation but rests in the minds of hydrogeologists. Indeed, only a profound insight in the combined hydrodynamical and hydrochemical aspects by a refined system analysis can provide the key to really understand what controls groundwater quality, also in coastal aquifers.

Keywords: natural groundwater quality in coastal aquifers, salinization/freshening, cation exchange, reaction-transport modelling

Introduction

Understanding natural groundwater quality controls in any aquifer should result from an integrated hydrogeological investigation (Figure 1), as hydrogeochemistry is tightly linked to hydrodynamics. Such study starts with a thorough characterization stage, in which existing data are collected, and necessary new data are acquired. Data concerned are related to aquifer geometry, hydraulic parameters of aquifers and adjacent aquitards, groundwater flow within aquifers and interaction amongst them, groundwater quality distribution and the effect of (over)exploitation on groundwater flow and chemistry.

Data analysis is performed in a system analysis, consisting of a hydrodynamical and a hydrochemical part. The hydrodynamical system analysis reveals the functioning of groundwater flow cycles with recharge and discharge areas, and allows to deduce groundwater flow velocities and the delimitation of well capture zones. The hydrochemical system analysis, by preference also including isotopic data, contributes to the understanding of the origin of groundwater chemistry, determined by end members and chemical processes, including interaction with the sediment (Custodio, 1987).

Integration of both parts of the system analysis leads to the conceptual model, which is tested in the subsequent mathematical modelling step. Finally, the calibrated model can be applied for management purposes, e.g. prediction of the response to new managing strategies, delimitation of protection zones and optimization of pumping scenarios.

UNDERSTANDING NATURAL GROUNDWATER QUALITY CONTROLS

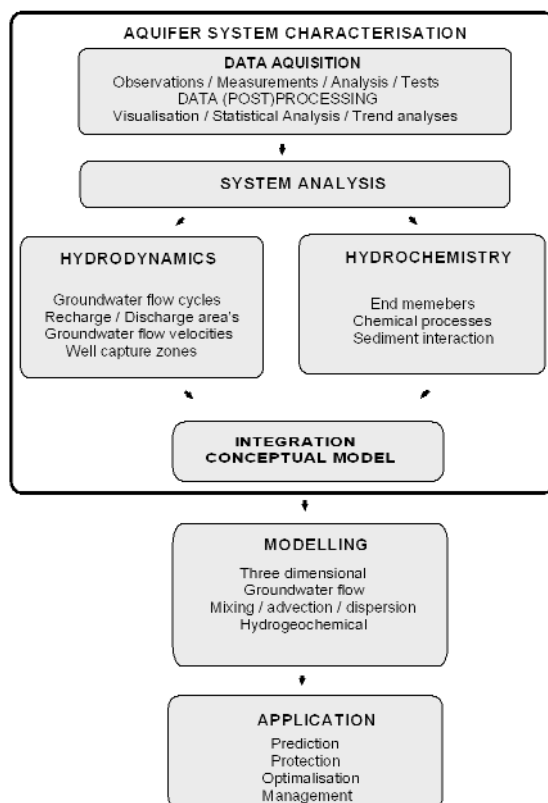


Figure 1. Understanding natural groundwater quality controls

Natural groundwater quality controls in coastal aquifers

Coastal aquifers are mostly characterized by the confrontation between marine and continental conditions. This may result in the salinization of fresh aquifers, or conversely, the freshening of saline aquifers.

Salinization can be induced by natural events, such as marine transgressions and flooding, or by anthropogenic causes, such as overexploitation of the aquifer. Freshening can have natural origins, such as the development of dune belts along the coastline, or it can be triggered by man by artificial recharge. Each of these mechanisms has its own time scale (Figure 2), and the present fresh/salt water distribution in a coastal aquifer is very often determined by the long-term hydrogeological and physiographical history of the region.

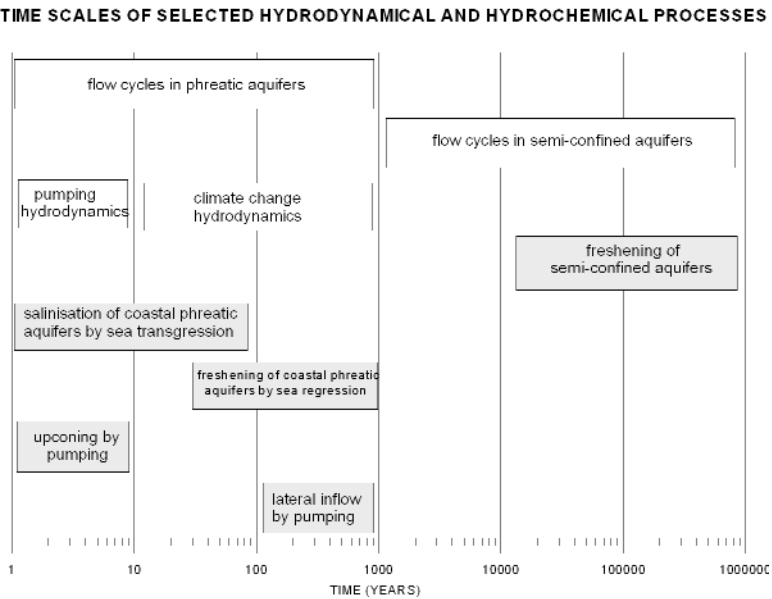


Figure 2. Timescales of selected hydrodynamic and hydrochemical processes

Phreatic aquifers react on shorter time scales, whereas semi-confined aquifers need more time to reach equilibrium with new conditions.

Besides, hydrochemistry needs more time to respond to a new equilibrium compared to hydrodynamics. This is related to hydrodynamics being one of the determining factors for hydrogeochemistry, because of the associated mass transport processes of advection and hydrodynamic dispersion. A new hydrodynamic equilibrium is reached fairly quickly, e.g. upon a marine regression, which is followed by the development of dune belts acting as recharge areas, and thus the establishment of a new flow regime. Yet, the associated freshening from the chemical point of view, will take very long to be completed. Still, in coastal aquifers, we have to deal with an additionally complicating factor, as the changing hydrogeochemistry (specifically the changing salt content) may influence hydrodynamics, with respect to the importance of density-driven flow. Moreover, also hydraulic conductivity can be affected as a result of the changing conditions as salinization or freshening proceed (Goldenberg, 1985).

Last but not least, freshening has a longer time scale upon which to act, than salinization. This has to do with the concentration difference between both, and the notion about "fresh" and "saline" water. A mixture of 95% fresh water (TDS: 375 mg/L) with only 5% seawater (TDS: 35,000 mg/L) produces fairly brackish water with a TDS of 2106 mg/L, which is certainly no longer recognized as "fresh". On the other hand, a mixture of 95% seawater with 5% fresh water has a TDS of 33,269 mg/L, and is considered salt without any reserve.

Salinization and freshening

When analyzing natural groundwater quality controls in coastal aquifers, one has to consider the specific role of the factors determining groundwater composition under salinizing or freshening conditions. These factors are:

- the composition (and mixing ratio) of end members
- hydrodynamics: mass transport processes
 - advection
 - hydrodynamic dispersion (mixing)
- chemical reactions
 - within the water phase
 - with the gas phase in the unsaturated zone
 - with the aquifer matrix

The end members to be considered in coastal aquifers are seawater and fresh recharge water, the latter generally conceived as infiltrating rain having dissolved calcite. The main ions in this recharge water result from calcite dissolution (Appelo and Postma, 1993), and the watertype is F-CaHCO₃0 according to the classification of Stuyfzand (1986). The seawater type is S-NaCl0. Besides the major ions, the classification name expresses the chloride content (fresh F: < 150 mg/L; fresh-brackish F_b: 150-300 mg/L; brackish B: 300-1000 mg/L; brackish-salt B_s: 1000-10,000 mg/L; salt S: 10,000-20,000 mg/L; hyperhaline H: > 20,000 mg/L) and the cation exchange code. The latter indicates either a surplus (+) of marine cations ($(\text{Na}^+ + \text{K}^+ + \text{Mg}^{2+})_{\text{corrected}} > (\frac{1}{2}\text{Cl}^-)^{1/2}$), or a cation exchange equilibrium (0) ($-(\frac{1}{2}\text{Cl}^-)^{1/2} \leq (\text{Na}^+ + \text{K}^+ + \text{Mg}^{2+})_{\text{corrected}} \leq (\frac{1}{2}\text{Cl}^-)^{1/2}$), or a deficit (-) of marine cations ($(\text{Na}^+ + \text{K}^+ + \text{Mg}^{2+})_{\text{corrected}} < -(\frac{1}{2}\text{Cl}^-)^{1/2}$). All concentrations are expressed in meq/L. The parameter $(\text{Na}^+ + \text{K}^+ + \text{Mg}^{2+})_{\text{corrected}}$ represents the marine cations in the sample that are not due to admixture of the seawater end member, and is calculated as the sum of measured marine cations, from which 1.061Cl⁻ is subtracted, the latter representing the marine cations in the end member fraction $(\text{Na}^+ + \text{K}^+ + \text{Mg}^{2+})/\text{Cl}^- = 1.061$ for mean ocean water). A surplus of marine cations (+) points to cation exchange resulting from freshening, whereas a deficit (-) indicates cation exchange caused by salinization. The end members by definition show cation exchange equilibrium (0).

Salinization (Figure 3) is induced as the new saline end member is introduced into the fresh-water saturated aquifer, and both end members move by advection. At their interface, mixing of both end members occurs by hydrodynamic dispersion. As admixture of the saline end member increases, the chloride concentration in the water is raised proportionally. The main chemical reaction is cation exchange, resulting in a deficit of marine cations and a surplus of the fresh-water cation Ca²⁺. This leads to the development of the Ca-Cl watertype (Figure 4), which is typical for salinization.

Freshening (Figure 3) is induced as the new fresh end member is introduced into the seawater saturated aquifer, and both end members move by advection. At their interface, mixing of both end members occurs by hydrodynamic dispersion. As admixture of the fresh end member increases, the chloride concentration in the water is reduced proportionally. The main chemical reaction is cation exchange, resulting in a surplus of marine cations and a deficit of the fresh-water cation Ca²⁺. This leads to the development of the NaHCO₃+ watertype (Figure 4), which is typical for freshening. But in a further freshening phase, also the MgHCO₃ watertype develops as a result of cation exchange (Walraevens, 1990).

2 END MEMBERS:	
recharge water: infiltrating rain dissolving calcite $F\text{-CaHCO}_3\text{O}$	seawater $S\text{-NaClO}$
SALINIZATION	
<ul style="list-style-type: none"><i>advection</i> will bring the new saline end member in the aquifer, and both end members will move with groundwater flowat the interface, both end members will be mixed by <i>dispersion</i> $F \rightarrow F_b \rightarrow B \rightarrow B_s \rightarrow S$the main chemical reaction will be <i>cation exchange</i> \Rightarrow deficit of marine cations (-) $\text{CaHCO}_3\text{O} \rightarrow \text{CaCl}^- \rightarrow \text{NaCl}^- \rightarrow \text{NaClO}$	

2 END MEMBERS:	
seawater $S\text{-NaClO}$	recharge water: infiltrating rain dissolving calcite $F\text{-CaHCO}_3\text{O}$
FRESHENING	
<ul style="list-style-type: none"><i>advection</i> will bring the new fresh end member in the aquifer, and both end members will move with groundwater flowat the interface, both end members will be mixed by <i>dispersion</i> $S \rightarrow B_s \rightarrow B \rightarrow F_b \rightarrow F$the main chemical reaction will be <i>cation exchange</i> \Rightarrow surplus of marine cations (+) $\text{NaClO} \rightarrow \text{NaCl}^+ \rightarrow \text{NaHCO}_3^+ \rightarrow \text{MgHCO}_3^+ \rightarrow \text{CaHCO}_3^+ \rightarrow \text{CaHCO}_3\text{O}$	

Figure 3. Factors changing groundwater quality as a result of salinization or freshening

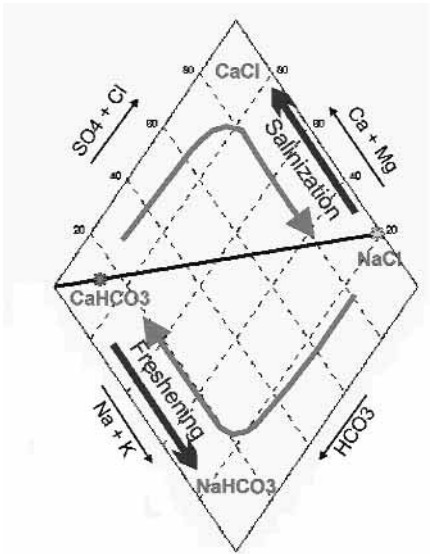


Figure 4. Piper diagram showing the shift in ion distribution due to salinization and freshening

As an example of the groundwater quality evolution resulting from freshening, the variation of groundwater quality in the Tertiary semi-confined Ledo-Paniselian aquifer in Flanders is presented (Walraevens, 1990). The aquifer consists of marine sands. In this well-documented aquifer, subsequent

strips of different watertypes occur, that stretch perpendicular to the direction of (pre-pumping) groundwater flow. In the downstream direction, groundwater quality is increasingly exhibiting the influence of the former marine conditions. The Na^+/Cl^- ratio is shown as a function of the Cl^- concentration in Figure 5. Chloride increases in the downflow direction. Dilution of the connate seawater is the first response to freshening. Cation exchange follows in a later stage. Upstream of the fresh/saline-water interface, Na^+ is strongly increased, resulting in the NaHCO_3 watertype, and a peak in the Na^+/Cl^- ratio. In a further phase of cation exchange, marine Mg^{2+} is desorbed from the sediment in exchange for Ca^{2+} , resulting in the MgHCO_3 watertype. As $\text{Ca}^{2+}/\text{Na}^+$ exchange has largely been completed by then, the Na^+/Cl^- ratio has returned to normal values, comparative to both end members. Finally, in the freshened recharge area, cation exchange is not playing a (determining) role any more, and the CaHCO_3 watertype is found.

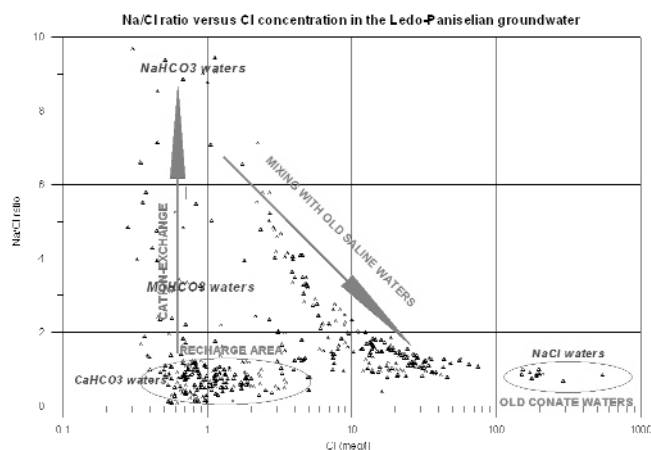


Figure 5. Na^+/Cl^- ratio versus Cl^- concentration in the Ledo-Paniselian groundwater

The importance of cation exchange reactions in conditions of salinization/freshening has for a long time been generally underestimated. The role of cation exchange during freshening was mostly thought to be restricted to the appearance of the NaHCO_3 watertype as a result of $\text{Ca}^{2+}/\text{Na}^+$ exchange. Increases in Mg^{2+} due to the subsequent $\text{Ca}^{2+}/\text{Mg}^{2+}$ exchange were frequently explained using solid carbonate reactions, for example for the Aquia aquifer in Maryland (Chapelle and Knobel, 1983, who attributed increased Mg^{2+} to dissolution of Mg -calcites and precipitation of pure calcite) and the Lincolnshire limestone in England (Bishop and Lloyd, 1990). Yet, Valocchi *et al.* (1981) had observed the chromatographic sequence of Na^+ , Mg^{2+} and Ca^{2+} dominated watertypes in a field experiment. The downstream K^+ -increase was e.g. evident in the Aquia aquifer, but not discussed by Chapelle and Knobel (1983). Appelo (1994) has emphasized and demonstrated cation exchange under freshening conditions, producing this chromatographic sequence, with sequential peaks of Na^+ , K^+ and Mg^{2+} , upstream of the salt/fresh-water boundary. He developed PHREEQM as a one-dimensional transport model, using PHREEQE (Parkhurst *et al.*, 1980) to calculate geochemical reactions, extending the latter to deal with ion exchange reactions. The code was developed further to yield PHREEQC (Parkhurst and Appelo, 1999), as the present standard for hydrogeochemical transport modelling.

Another important consequence of cation exchange reactions is their effect on the saturation index of minerals, specifically of calcite. In freshening conditions, Ca^{2+} is depleted in groundwater, allowing for a second stage of calcite dissolution, which may lead to the high HCO_3^- concentrations that are typical for the NaHCO_3 watertype (Walraevens, 1990). In conditions of salinization, Ca^{2+} is increased in groundwater, which may lead to supersaturation and precipitation of calcite. The preliminary recognition of these processes is supported by calculating the conservative mixture based on the chloride concentration, and proposing chemical reactions explaining the difference with the sample composition (Appelo and Postma, 1993).

Modelling groundwater quality in coastal aquifers

Modelling is an important tool in understanding how aquifer systems work. Until recently, hydrodynamical and hydrochemical aspects were tackled separately, with different models.

Yet, in order to simulate the evolution in the changing environment of coastal aquifers, where salinization or freshening are going on, it is indispensable to have a combination of transport and reactions within the model. Mass balance models, as NETPATH (Plummer *et al.*, 1991), cannot be successfully applied, because the groundwater composition at a given point within the aquifer is transient, related to the changing composition of the sorbed cations on the exchange sites in the upstream part.

Hydrodynamic models for coastal aquifers are typically incorporating density-driven flow. Two groups of hydrodynamic models can be considered. The first group is neglecting reactions: the sharp interface models consider only advection, e.g. SHARP (Essaid, 1990); the solute transport models deal with both advection and dispersion, e.g. HST3D (Kipp, 1987), MOCDENS3D (Oude Essink, 1998) and SEAWAT (Guo *et al.*, 2002). The second group handles a very simple approach for compositional changes, using a sink/source term, e.g. MT3D (Zheng, 1990).

On the other hand, hydrochemical aspects have been investigated with hydrogeochemical models based on speciation and a reaction scheme. In the first generation of hydrogeochemical models, groundwater flow and transport were not taken into account. Well-known examples of this group are WATEQ (Truesdell and Jones, 1974), MINTEQ (Krupka, 1992) and PHREEQE (Parkhurst *et al.*, 1980). In a further step of development, groundwater flow and transport were considered in a very simplified approach (one-dimensional along a path-line): PHREEQM (Appelo, 1994) and PHREEQC (Parkhurst and Appelo, 1999) illustrate this category. Figure 6 is an example of the application of PHREEQM, showing modeled and measured concentrations of main ions in the Ledo-Paniselian aquifer along a flow line, starting at the recharge area (Walraevens and Cardenal, 1999). Downstream increasing Cl^- and SO_4^{2-} concentrations show the growing admixture of the saline end member. Also Na^+ exhibits this effect, but additionally, Na^+ is increased upstream of the fresh/saline-water interface, as a result of cation exchange. Further upstream, also K^+ peaks due to cation exchange, and subsequently, Mg^{2+} is raised by the same process. Finally, in the most upstream waters, the effect of cation exchange has been reduced, and Ca^{2+} concentrations are no longer lowered by its effect. Notice the difference in concentration scales: Na^+ is more strongly raised by cation exchange than K^+ and Mg^{2+} are.

At this moment a new generation of simulation models is showing up that couples three dimensional flow and transport with hydrogeochemical calculations. This kind of models should be able to simulate complete groundwater composition (major and minor elements and species) in real aquifer flow conditions. An example of such a model is PHAST (Parkhurst *et al.*, 2004). PHAST is a 3-dimensional multicomponent reaction-transport model that can be used to simulate transient groundwater flow with geochemical reactions. The reaction-transport equations are solved by using the sequential approach in which transport and reaction are divided into separate calculations for each time step. First the components are transported and then geochemical reactions are calculated. The solute-transport simulator HST3D is used for the transport calculations and the program PHREEQC is used for the geochemical calculations.

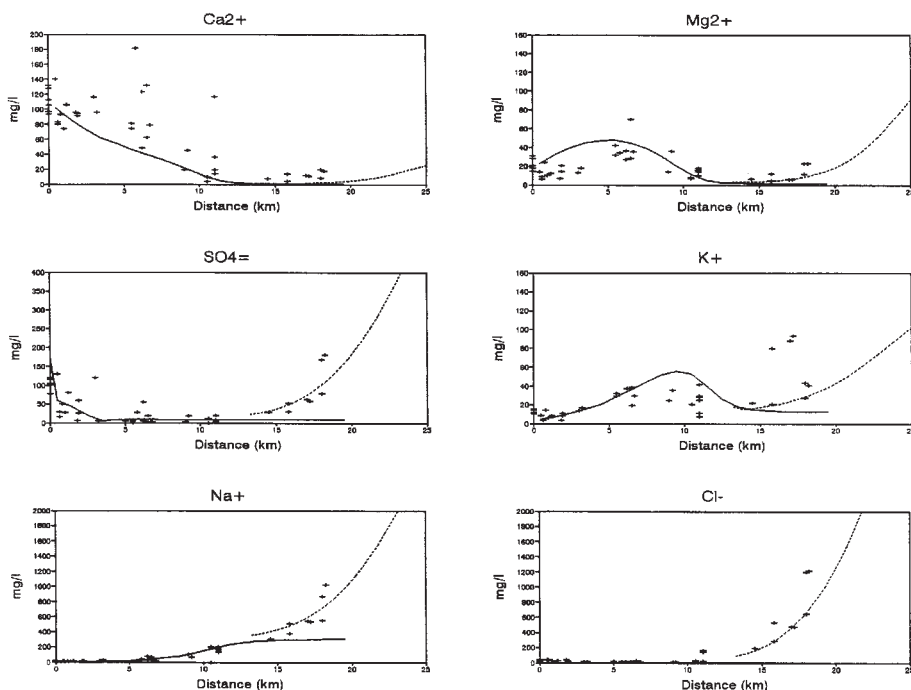


Figure 6. Changing ion concentrations in the Ledo-Paniselian aquifer along a flow line, with increasing distance from the recharge area. Crosses represent measured concentrations. Solid and dashed lines are modeled concentrations (Walraevens and Cardenal, 1999).

The geochemical part of the program has the capability to perform a wide range of chemical reaction calculations that include aqueous complexation, mineral equilibria, surface complexation, ion exchange, solid-solution equilibria, gas-phase equilibration, and general kinetic reactions. In addition, geochemical simulations, which include all of these types of reaction calculations plus mixing, irreversible reactions, and temperature variation, may be used to define initial and chemical boundary conditions for the reaction-transport simulations.

Considering all these possibilities, PHAST can be used to study saltwater intrusion problems. It can treat cation exchange processes with multiple cations and mineral equilibria like calcite dissolution caused by

cation exchange. But it can handle a much wider scope of processes allowing e.g. the incorporation of redox species and reactions, or adsorption of ions on hydroxides by surface complexation.

As an example of the capabilities of PHAST, it has been used to simulate the freshening of a dune belt. The shown example is schematic but representative for the development of the dune belt along the Belgian coast, which provides the most important aquifer system for drinking water production in the coastal region. We have tried to simulate the occurrence and evolution of the genetic sequence of watertypes produced by freshening (Figure 3) during the whole lifetime of the dunes, starting from the initial onset of development when the aquifer system was still filled with seawater (that had infiltrated during previous marine transgressions), until the nowadays present-day situation, in which a fresh-water lens of CaHCO_3 waters is present under the dunes, while at the transition zone between dunes and inland polders fresh MgHCO_3 and brackish NaHCO_3 waters are present. Under the polders fossil seawater is still present and saline NaCl waters are encountered.

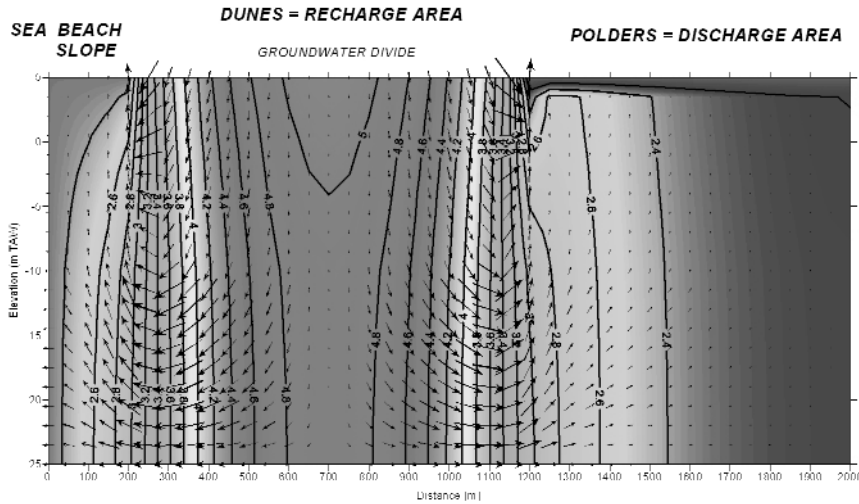


Figure 7. Calculated heads and flow vectors

The coastal Quaternary aquifer is around 30 m thick and consists of sandy marine deposits. The dune belt is usually between 1 and 2 km wide. Average annual recharge in the dunes is around 250 to 270 mm. The PHAST simulation is two-dimensional along a profile perpendicular to the coastline, starting at the shoreline, crossing the beach slope, dune belt and part of the inland polder region. Total length is 2 km of which the dunes occupy 1 km. The dune belt acts as a groundwater divide with one flow cycle discharging to the sea, the other to the inland polders (Figure 7). In the modeled profile the hydrodynamical boundary conditions were chosen according to this flow situation with recharge in the dunes, defined heads at the shoreline and on the beach slope, and drains in the polders. Hydrochemically the initial condition is an aquifer system filled with seawater (standard seawater composition). The aquifer recharge water (in the dunes) is generated by equilibrating pure water with atmospheric CO_2 (partial pressure 0.01 atm) and calcite (until saturation). Cation exchange capacity (CEC) of the marine sands is 5 meq/100 g and the exchange complex is initially equilibrated with seawater reflecting the initial marine conditions.

Model chemical output includes total element (e.g. Na, K, Mg, Ca, Cl) and species (e.g. HCO_3^-) concentrations, but also composition of the exchange complex (adsorbed cations) and mineral saturation indices (e.g. for calcite). These parameter distributions can be plotted on profiles, and from the whole groundwater composition in each model cell the groundwater type can be derived using Stuyfzand's (1986) classification scheme. Then the calculated distribution of watertypes can be visualized and compared with observations. Visual examples of model output are presented in figures 8 to 11. Chloride concentrations (Figure 8) are only affected by advection and dispersion because Cl^- is a conservative parameter. The freshening under the dune belt is clearly visible with a small more brackish lens persisting underneath the groundwater divide. The concentrations of main cations are, besides the mixing ratio of the original two end members, also altered by the cation exchange process. This produces at first NaHCO_3 water (in which calcium is replaced by sodium) and later MgHCO_3 water (in which calcium is replaced with magnesium). From the concentrations of the main ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} and HCO_3^-) the groundwater type was calculated (Figure 9). Initially during the freshening process, NaHCO_3 water appears under the dunes (not the CaHCO_3 water that infiltrates), followed by MgHCO_3 water and only finally, after the exchange complex has lost its adsorbed Na^+ and Mg^{2+} , CaHCO_3 waters show up. This cation exchange is also recognized if the Na^+/Cl^- ratio for each model cell is plotted versus the Cl^- concentration. Then a rise of the ratio is recognized for the NaHCO_3 waters (Figure 10), corresponding with the pattern of measured values for the Ledo-Paniselian aquifer (Figure 5). Also, as a result of the replacement of calcium by sodium, the groundwater becomes undersaturated with respect to calcite (Figure 11), as indicated by the negative saturation index values. Where this happens, dissolution of calcite can occur and bicarbonate levels will increase significantly. This is typical for the NaHCO_3 waters.

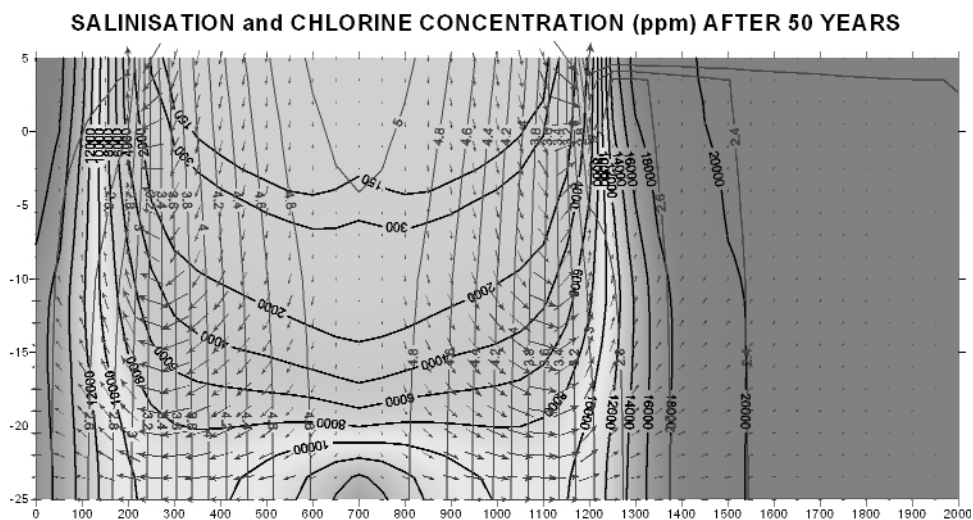


Figure 8. Calculated chloride concentrations after 50 years

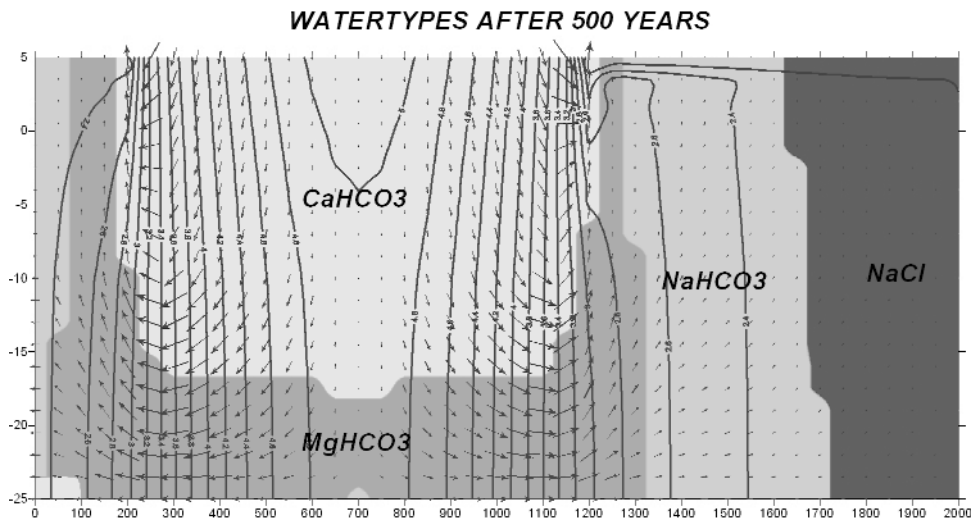


Figure 9. Calculated distribution of groundwater types after 500 years

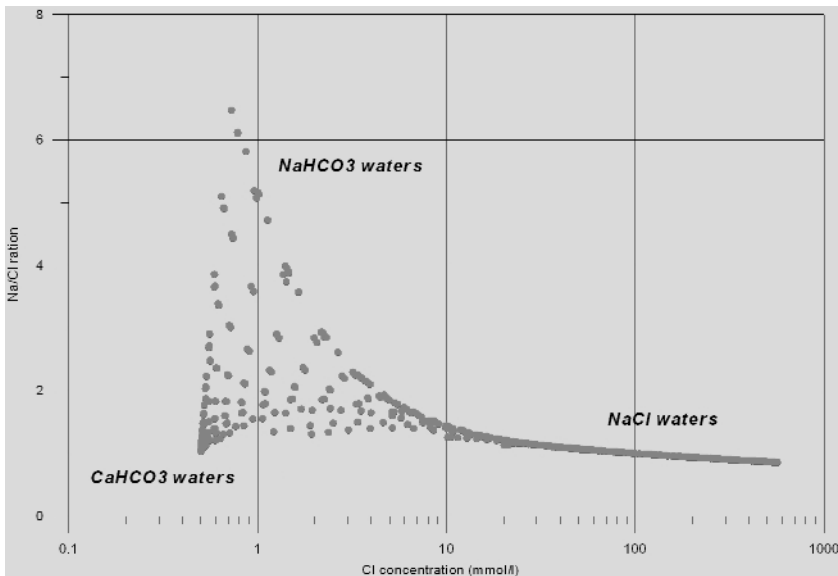


Figure 10. Calculated ratio of Na/Cl versus Cl in the model cells

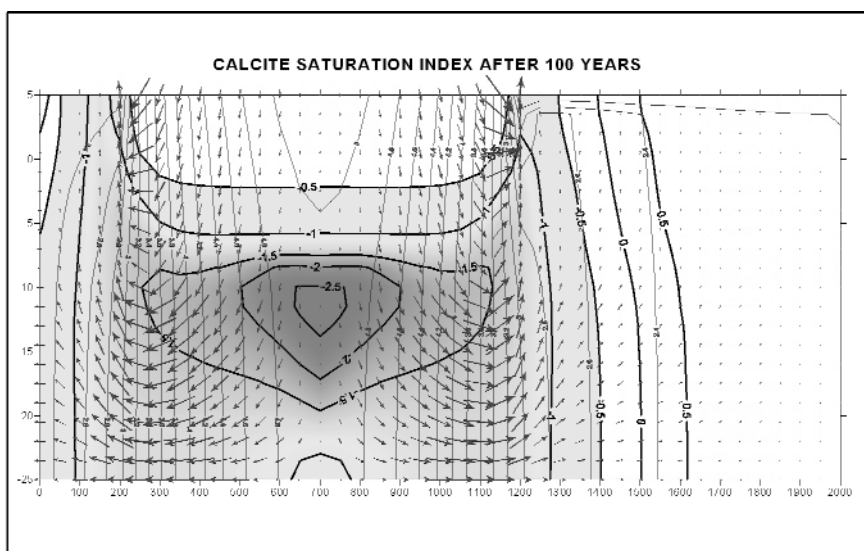


Figure 11. Calculated calcite saturation index after 100 years of freshening

This example shows that with models like PHAST, field cases with complicated hydrodynamics, consisting of multiple flow cycles, and complex hydrochemistry, including processes like mineral dissolution (and/or precipitation) and cation exchange, can be simulated and can help us to understand the natural groundwater quality controls. In the dynamic changing environments of coastal aquifers, the availability of such a tool constitutes definitely a progress.

Conclusions

The integration of the study of hydrodynamics and hydrogeochemistry is for coastal aquifers even more important than for other aquifers, because of their strong mutual interaction. In the past, both aspects have been mostly dealt with separately. Recently, advances are being made in understanding natural groundwater quality controls in coastal aquifers, using the new generation of simulation models that couple three-dimensional flow and transport with hydrogeochemical calculations. This tool will contribute to the wider recognition of the role of cation exchange, which is larger than is generally acknowledged today. Upon freshening, a chromatographic sequence of subsequently desorbed marine cations (Na^+ , K^+ and Mg^{2+} , in this order) gives rise to consecutive concentration peaks. Cation exchange also has an important effect on calcite saturation: in freshening conditions, the resulting undersaturation allows for a second stage of calcite dissolution, producing high HCO_3^- concentrations in the NaHCO_3 watertype; in salinizing conditions, supersaturation may lead to calcite precipitation.

The use of these new models needs to be based on good and sufficient field data, without which the reliability of the model is uncertain. For the profound insight into the functioning of the dynamic, changing environment of coastal aquifers, the availability of these new modelling tools combined to sufficient good-quality data, constitutes definitely a progress. It will allow to improve our process understanding, which

should be the basis for aquifer management, with respect for the uniqueness of each individual aquifer.

References

- APPELO, C.A.J. (1994). Cation and proton exchange, pH variations, and carbonate reactions in a freshening aquifer. *Water Resour. Res.* 30(10), 2793-2805.
- APPELO, C.A.J. and POSTMA, D. (1993). *Geochemistry, groundwater and pollution*. 536 p. Balkema, Rotterdam.
- BISHOP, P.K. and LLOYD, J.W. (1990). Chemical and isotopic evidence for hydrogeochemical processes occurring in the Lincolnshire limestone. *J. Hydrol.* 212, 293-320.
- CHAPELLE, F.H. and KNOBEL, L.L. (1983). Aqueous geochemistry and exchangeable cation composition of glauconite in the Aquia aquifer, Maryland. *Ground Water* 21, 343-352.
- CUSTODIO, E. (1987). Hydrogeochemistry and tracers. In: CUSTODIO, E. and BRUGGEMAN, G.A. (eds.) *Groundwater problems in coastal areas. Studies and reports in Hydrology* 45, 213-269. UNESCO-PHI, Paris.
- ESSAID, H.I. (1990). A multilayered sharp interface model of coupled freshwater and saltwater flow in coastal systems: model development and application. *Water Resour. Res.* 26(7), 1431-1454.
- GOLDENBERG, L.C. (1985). Decrease of hydraulic conductivity in sand at the interface between seawater and dilute clay suspensions. *J. Hydrol.* 78, 183-199.
- GUO, WEIXING and LANGEVIN, C.D. (2002). User's Guide to SEAWAT: A Computer Program for Simulation of Three-Dimensional Variable-Density Ground-Water Flow: *Techniques of Water-Resources Investigations Book 6, Chapter A7*, 77 p. USGS, Washington DC.
- KIPP, K.L. (1987). HST3D: A computer code for simulation of heat and solute transport in three-dimensional groundwater flow systems. *U.S. Geological Survey Water-Resources Investigations Report* 86-4095, 517 p. USGS, Washington DC.
- KRUPKA, K.M. (1992). MINTEQ. Aqueous Geochemical Equilibria Studies. Technical Report ESTSC/NRC--000082DVX1100; NES-1101. *Batelle Pacific Northwest Lab, Richland, WA (United States)*.
- OUDE ESSINK, G.H.P. (1998). MOC3D adapted to simulate 3D density-dependent groundwater flow. *Proc. MODFLOW'98 Conf., Golden, Colorado, USA*, 291-303.
- PARKHURST, D.L. and APPELO, C.A.J., (1999). User's guide to PHREEQC (Version 2) – a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p. USGS, Washington DC.
- PARKHURST, D.L., THORSTENSON, D.C. and PLUMMER, L.N. (1980). PHREEQ – a computer program for geochemical calculations. *U.S. Geological Survey Water-Resources Investigations Report* 80-96, 195 p. (Revised and reprinted, 1990). USGS, Washington DC.
- PARKHURST, D.L., KIPP, K.L., ENGESGAARD, P. and CHARLTON, S.R., (2004). PHAST - A Program for Simulating Ground-Water Flow and Multicomponent Geochemical Reactions. *USGS. Program Manual*. (http://www.brr.cr.usgs.gov/projects/GWC_coupled/phast)
- PLUMMER, L.N., PRESTEMON, E.C. and PARKHURST, D.L., 1991, An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH: U.S. Geological Survey Water-Resources Investigations Report 91-4078, 227 p. USGS, Washington DC.
- STUYFZAND, P.J. (1986). A new hydrochemical classification of watertypes: Principles and application to the coastal dunes aquifer system of the Netherlands. *9th Salt Water Intrusion Meeting, Delft 1986. Proceedings*. 641-655.
- TRUESDELL, A.H. and JONES, B.F. (1974). WATEQ, a computer program for calculating chemical equilibria of natural waters. *Journ. Research U.S. Geol. Survey* 2(2), 233-248.

- VALOCCHI, A.J., STREET, R.L. and ROBERTS, P.V. (1981). Transport of ion-exchanging solutes in groundwater: Chromatographic theory and field simulation. *Water Resour. Res.* 17, 1517-1527.
- WALRAEVENS, K. (1990). Hydrogeology and hydrochemistry of the Ledo-Paniselian semi-confined aquifer in East- and West-Flanders. *Acad. Analecta* 52, 3, 11-66.
- WALRAEVENS, K. and CARDENAL, J. (1999). Preferential pathways in an Eocene clay: Hydrogeological and hydrogeochemical evidence. *Muds and Mudstones: Physical and Fluid Flow Properties. Geological Society of London, Special Publications* 158, 175-186.
- ZHENG, C. (1990). *MT3D*, A modular three-dimensional transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater system. *Report to the Kerr Environmental Research Laboratory, US Environmental Protection Agency, Ada, OK.*